

A new reduced molybdenum oxide with a hollandite-type structure, $\text{PrMo}_6\text{O}_{12}$

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Key indicators

Single-crystal X-ray study

$T = 293 \text{ K}$

Mean $\sigma(\text{P-O}) = 0.003 \text{ \AA}$

R factor = 0.032

wR factor = 0.081

Data-to-parameter ratio = 27.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, praseodymium hexamolybdenum dodecaoxide, $\text{PrMo}_6\text{O}_{12}$, crystallizes in the tetragonal space group $I4/m$ and is isostructural with $\text{NdMo}_6\text{O}_{12}$. Both compounds adopt a hollandite-related structure with a tripled c axis compared to the mineral hollandite. Within the double chains of edge-sharing MoO_6 octahedra, the Mo atoms form infinite chains of Mo_3 triangular clusters. Another dominant feature of the structure is the ordering of the Pr^{3+} cations within the square-shaped channels delimited by the Mo—O double strings.

Comment

Compounds which crystallize in the hollandite-type structure have been the subject of numerous researches because of the possibility of one-dimensional ionic conductivity through the tunnel on the one hand, and on the other hand, that of their use as host materials for the storage of radioactive wastes. From the crystallographic point of view, these phases frequently exhibit complex commensurate or incommensurate superstructures due to partial occupation and ordering of the A cation within the four-sided tunnels. Reduced molybdenum oxides which crystallize with a hollandite-type structure are in addition characterized by a clustering of the Mo atoms which results in the formation of tetrameric molybdenum Mo_4 clusters in $\text{K}_2\text{Mo}_8\text{O}_{16}$ (Torardi & Calabrese, 1984) and $\text{Ba}_{1.14}\text{Mo}_8\text{O}_{16}$ (Torardi & McCarley, 1981) synthesized by solid-state reaction, and Mo_3 triangles in $\text{La}_{1.16}\text{Mo}_8\text{O}_{16}$ (Leligny *et al.*, 1992) and $\text{NdMo}_6\text{O}_{12}$ (Tortelier *et al.*, 1998) obtained by fused-salt electrolysis. While in $\text{K}_2\text{Mo}_8\text{O}_{16}$ all square-prismatic sites are occupied, a partial occupation and disorder of the large cations occur in the Ba compound. For $\text{La}_{1.16}\text{Mo}_8\text{O}_{16}$, a one-dimensional incommensurate modulated structure with a modulation wavevector of $q^* = 0.608c^*$ was determined. We report here the single-crystal structure determination of a new reduced ternary oxide of molybdenum which adopts the hollandite-type structure, namely $\text{PrMo}_6\text{O}_{12}$.

$\text{PrMo}_6\text{O}_{12}$ crystallizes in a hollandite-type structure with a tripled c axis due to the ordering of the cations in the tunnels. The Mo—O framework of $\text{PrMo}_6\text{O}_{12}$ consists of double-rutile chains of edge-sharing MoO_6 octahedra with each octahedron sharing four edges with four other neighboring octahedra. Within each chain, the Mo atoms that are displaced from the center of their octahedral oxygen environment, form infinite metallic chains based on Mo_3 triangular clusters, as shown in Fig. 1. These double strings which run parallel to the c axis are then linked together by sharing sp^2 -type O-atom corners to form large square tunnels of 2×2 octahedra in cross-section in which the Pr^{3+} ions are located (Fig. 2a) as well as smaller sized channels similar to those found in the rutile-type struc-

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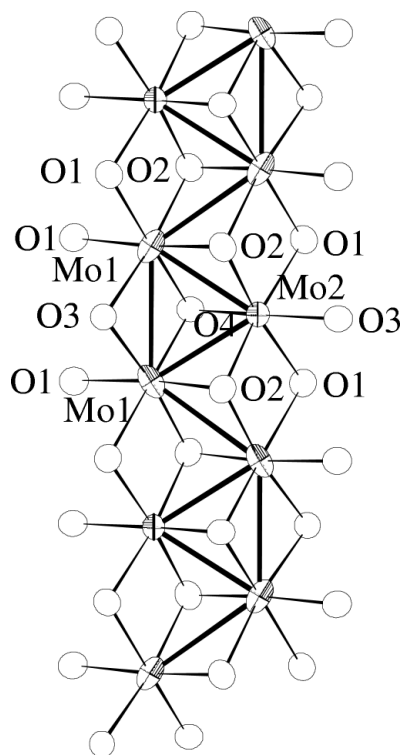


Figure 1
Section of the metal-oxide chains in $\text{PrMo}_6\text{O}_{12}$. Mo–Mo bonds are represented by solid black lines. Displacement ellipsoids are drawn at the 97% probability level.

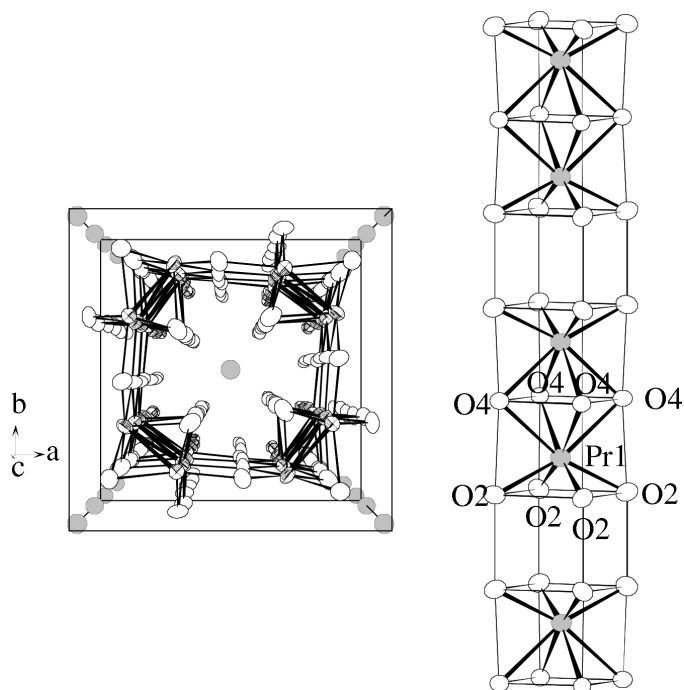


Figure 2
(a) View of the $\text{PrMo}_6\text{O}_{12}$ structure along the tetragonal c axis. (b) A view perpendicular to the c axis of $\text{PrMo}_6\text{O}_{12}$ showing the ordered arrangement of the Pr^{3+} cations within a channel.

ture. The Mo–Mo distances within the Mo_3 triangles are 2.5589 (5) Å for the two diagonal bonds Mo1–Mo2, and

2.7381 (7) Å for the Mo1–Mo1 bond parallel to the c axis. The shortest distance between triangles is 2.7344 (7) Å and corresponds to the diagonal bond Mo1–Mo1. The other two intertriangle Mo1–Mo2 distances that are parallel to the c axis are 2.9573 (4) Å and thus are only weakly bonding.

As previously observed in the other hollandite-related reduced molybdenum oxides, the O atoms can be divided into two different types: O1 and O3 which interconnect the double chains and are linked in trigonal planar-like coordination to three Mo atoms, and O2 and O4 that bridge three Mo atoms of the same double chain and are also bonded to one (O2) or two Pr atoms (O4). The Mo–O bond lengths vary from 1.996 (3) to 2.052 (3) Å for the O atoms of the former type, and from 2.064 (3) to 2.102 (3) Å for those of the second type. From the Mo–O bond lengths, the valences of the two crystallographically independent Mo atoms calculated by using the relationship of Brown & Wu (1976) [$s = (d_{\text{Mo-O}}/1.882)^{-6.0}$] are +3.53 (3) and +3.64 (3), respectively. This yields an average value of +3.57 (3), in reasonably good agreement with the expected value of +3.5. The Pr^{3+} ions occupy, in an ordered way, two out of the three possible square-prismatic sites formed by the intrachain O atoms (Fig. 2b). In order to minimize Pr^{3+} – Pr^{3+} Coulomb repulsions, the Pr^{3+} ions of two consecutive sites are shifted away from one another along the [001] direction. Consequently, each Pr^{3+} ion is displaced by 0.368 Å from the center of its tetragonal prismatic site and thus has four nearest O atoms at 2.401 (3) Å and four furthest ones at 2.688 (3) Å. The average Pr–O bond distance is 2.54 Å that is slightly larger than the value of 2.51 Å expected from the sum of the ionic radii of Pr^{3+} (CN8) and O^{2-} (CN4) (Shannon & Prewitt, 1969). The distance between two close Pr^{3+} ions is 3.589 (1) Å.

Experimental

Single crystals of $\text{PrMo}_6\text{O}_{12}$ were obtained by the electrolysis of a melt formed at 1233 K from a mixture of Rb_2MoO_4 , MoO_3 and Pr_6O_{11} having the molar ratio 25:15:1. The electrolysis was carried out in air using an alumina crucible. The anode was a platinum foil with a surface area of about 1 cm² and the cathode a 10-turn spiral platinum made from a 0.4 mm diameter wire. At the end of the run, the electrodes were raised above the melt to allow them to cool rapidly to room temperature. Crystals which grow perpendicularly to the cathode in the form of black needle-shaped square prisms with the needle axis parallel to the tetragonal c axis (maximum dimensions 0.8 × 0.8 × 5 mm) were obtained by applying a constant current of 36 mA for 12 h. Single crystals were separated from the matrix and the cathode by repeated and alternate washings in hot dilute solutions of potassium carbonate and hydrochloric acid.

Crystal data

$\text{PrMo}_6\text{O}_{12}$
 $M_r = 908.55$
Tetragonal, $I4/m$
 $a = 9.9147$ (3) Å
 $c = 8.6508$ (6) Å
 $V = 850.38$ (7) Å³
 $Z = 4$
 $D_x = 7.095$ Mg m^{−3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
 $\theta = 10.3$ – 31.4°
 $\mu = 14.25$ mm^{−1}
 $T = 293$ (2) K
Parallelepiped, black
0.290 × 0.025 × 0.022 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 θ – 2θ scans
 Absorption correction: numerical (Coppens, 1970)
 $T_{\min} = 0.340$, $T_{\max} = 0.768$
 1494 measured reflections
 1385 independent reflections
 1242 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$
 $\theta_{\text{max}} = 40.0^\circ$
 $h = 0 \rightarrow 17$
 $k = 0 \rightarrow 17$
 $l = 0 \rightarrow 15$
 3 standard reflections
 frequency: 60 min
 intensity decay: <1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.081$
 $S = 1.18$
 1385 reflections
 50 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0281P)^2 + 24.9952P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 3.40 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -2.99 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.00110 (9)

Table 1

Selected geometric parameters (\AA).

Pr1–O2	2.401 (3)	Mo1–Mo2 ^v	2.5589 (5)
Pr1–O4	2.688 (3)	Mo1–Mo1 ^v	2.7344 (7)
Mo1–O3 ⁱ	1.996 (3)	Mo1–Mo1 ^{vi}	2.7381 (7)
Mo1–O1 ⁱⁱ	2.017 (3)	Mo1–Mo2	2.9573 (4)
Mo1–O1 ⁱ	2.052 (3)	Mo2–O1 ⁱ	2.012 (3)
Mo1–O2 ⁱⁱⁱ	2.085 (3)	Mo2–O3 ^{vii}	2.036 (4)
Mo1–O4 ^{iv}	2.101 (3)	Mo2–O2 ^{viii}	2.064 (3)
Mo1–O2 ⁱ	2.102 (3)	Mo2–O4 ^{ix}	2.092 (4)

Symmetry codes: (i) $\frac{1}{2} + y, -\frac{1}{2} - x, -\frac{1}{2} - z$; (ii) $1 - x, -1 - y, z$; (iii) $-y, x - 1, z$; (iv) $\frac{1}{2} - x, -\frac{1}{2} - y, -\frac{1}{2} - z$; (v) $\frac{1}{2} - x, -\frac{3}{2} - y, -\frac{1}{2} - z$; (vi) $x, y, -1 - z$; (vii) $1 - x, -1 - y, -z$; (viii) $\frac{1}{2} + y, -\frac{1}{2} - x, \frac{1}{2} + z$; (ix) $x, y - 1, z$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *MolEN* (Fair, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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